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Dynamic Viscoelasticity of End-Linking α, ω -Dihydroxyl Polybutadiene Solutions near the Gel Point

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Dynamic viscoelasticity of α, ω -dihydroxyl polybutadiene solutions was studied through gelation process by end-linking reaction. The gel point was determined as the reaction time $t=t_g$, at which the storage and the loss shear moduli, $G'(\omega)$ and $G''(\omega)$, became both proportional to ω^n over the whole range of the angular frequency ω measured. The critical behavior of the solutions near the gel point was discussed in terms of the exponent n , $\tan \delta$, the steady viscosity, and the equilibrium modulus.

KEY WORDS: Dynamic viscoelasticity/ End-linking polymer/ Gelation/ Critical exponent

1. INTRODUCTION

It seems well established that dynamic viscoelasticity is a powerful method for a study of the critical behavior of gelling systems.¹⁻¹⁷⁾ The gel point can be directly determined through the gelation process as the reaction time, $t=t_g$, at which the storage and the loss shear moduli, $G'(\omega)$ and $G''(\omega)$, become both proportional to ω^n over the wide range of the angular frequency ω . We can also estimate two characteristic quantities, the steady viscosity η before the gel point and the equilibrium shear modulus G_{eq} after the gel point using this method. The critical behavior of the systems near the gel point is then examined in terms of critical exponents, k and z , defined by following power laws,^{11,13)}

$$\eta \sim (|t-t_g|/t_g)^{-k} \sim \varepsilon^{-k} \quad (1)$$

$$G_{eq} \sim \varepsilon^z, \quad (2)$$

respectively. Here ε expresses the relative distance from the gel point.

In a previous work,¹⁸⁾ we studied effects of polymer molecular weight M and concentration C on dynamic viscoelasticity of α, ω -dimethylsilyl poly (propylene oxide) solutions through gelation process by end-linking. The three exponents, n , k , and z , were found to take universal values of $n=0.66 \pm 0.02$, $k=1.0 \pm 0.1$, and $z=2.0 \pm 0.1$ irrespective of M and C for unentangled prepolymer solutions. The presence of entanglement coupling in the prepolymer solution, on the other hand, made the critical behavior of η and G_{eq} obscure, and also affected the exponent values.

In order to examine whether this kind of universality holds for another system, we measured dynamic viscoelasticity of α, ω -dihydroxyl polybutadiene solutions through the gelation process by end-linking. A tri-functional crosslinker was used for chemical crosslinking reaction. The

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preliminary results are reported here.

2. EXPERIMENTAL

2.1 Materials

The polymer used in this study is α, ω -dihydroxyl polybutadiene (HTPB) kindly supplied from Japan Synthetic Rubber Co. The number average molecular weight M_n is 2,900 and the functionality is 2.15. The bulk polymer contained about 1% of 2,2'-methylene bis-(4-methyl 6-*t*-butyl phenol) as antioxidant. A mixture of ethylacetate and Desmodure REF (DRFE, Bayer AG) with three isocyanate groups was dried in vacuum and the white powder of DRFE obtained was used as crosslinker. Special grade *p*-xylene (Nacalai Tesque) was used as solvent without further purification.

The solutions were prepared by dissolving, DRFE in *p*-xylene, adding HTPB, and then stirring vigorously at room temperature. The polymer concentration was determined by weighing and the molar ratio of the two functional groups, $r = [\text{NCO}]/[\text{OH}]$ was adjusted to unity.

2.2 Method

The storage and the loss shear moduli, $G'(\omega)$ and $G''(\omega)$, of the solutions were measured in the angular frequency ω range from 0.30 to 99.9 rad/s at $25.0 \pm 0.1^\circ\text{C}$ using a stress-controlled rhometer (Carri-MED CSL-100) with a 4 cm parallel-plate configuration. Time evolution of the dynamic shear modulus through the gelation process was pursued by assuming that the reaction was initiated when HTPB was added.

3. RESULTS AND DISCUSSION

3.1 Determination of the gel point

Figure 1 shows changes in the frequency dependence of G' and G'' of the 30 wt% HTPB solution as end-linking of polymer proceeds by the tri-functional crosslinker DRFE. The data are shifted along the horizontal axis by a factor of 10^a in order to avoid data overlapping. At $t = 320$ and 400 min, G' and G'' are proportional to ω^2 and ω^1 over the measured ω range, respectively, indicating that the sample remains a viscous fluid. The viscoelastic behavior of the sample rather abruptly changes near the gel point $t = t_c$ as is exemplified by the data at $t = 420$ min. At $t = t_c$, G' and G'' should become both proportional to ω^n over the whole ω range.^{1,2)} The data at $t = 420$ min show that the solution just exceeded the critical gel point. The plateau appears in the G' vs. ω curve after t_c at the low ω end, and the gel can be characterized by the equilibrium modulus G_{eq} . The steady viscosity η is a characteristic quantity of the solution before t_c .

The gel point or t_c is more accurately determined from examination of time evolution of $\tan \delta (\equiv G''/G')$ at various frequencies. Figures 2 and 3 give plots of $\tan \delta$ against t for the two samples with the lowest and the highest polymer concentrations of 30 and 80 wt%, respectively. The proportionality of G' and G'' to ω^n means that $\tan \delta$ must take a same value at all ω values. The Kramers-Kronig relationship⁴⁾ gives that $\tan \delta$ and n are interrelated by eq (3),

$$\tan \delta = \tan (n\pi/2), \quad (3)$$

which is useful for an estimate of n . As is clear from the figures, the four curves obtained at $\omega =$

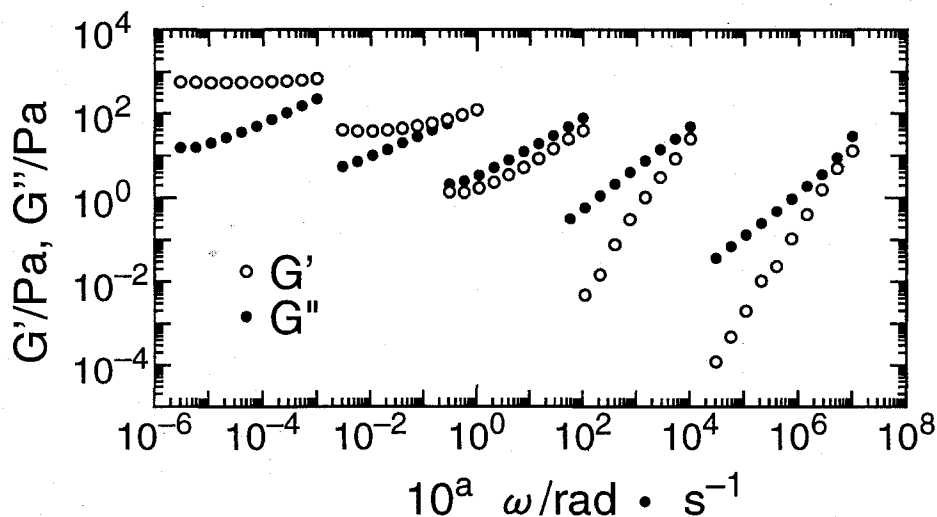


Fig. 1. Changes in the angular frequency dependence of $G'(\omega)$ and $G''(\omega)$ of the 30 wt% polybutadiene solution with the reaction time t . The data are shifted along the horizontal axis by 10^a in order to avoid data overlapping. From right to left: $t=320$ min and $a=4$; $t=370$ and $a=2$; $t=420$ and $a=0$; $t=470$ and $a=-2$; $t=520$ min and $a=-4$.

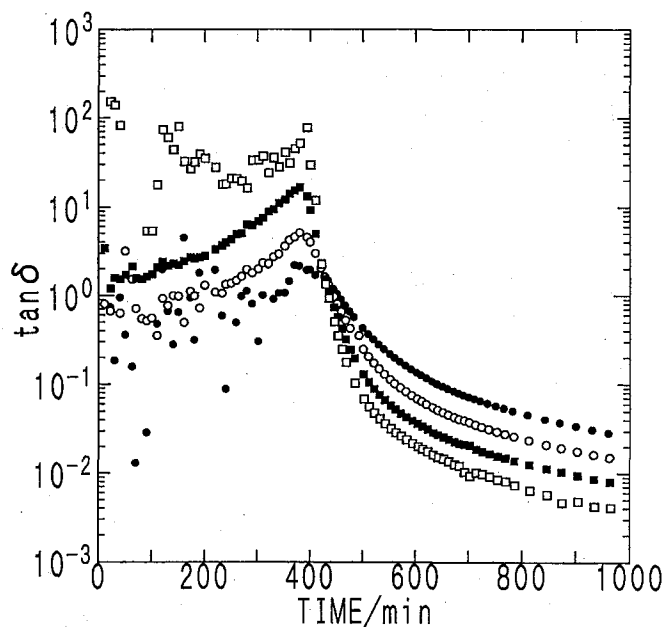


Fig. 2. Time evolution of $\tan \delta$ of the 30 wt% HTPB solution at four angular frequencies of $\omega=2.08$ (□), 7.56 (■), 27.5 (○), and 99.9 (●). Four curves meet at the critical time t_c .

2.01, 7.56, 27.5, and 99.9 rad/s meet at one point in the measured ω range. Thus this type of plot provides more accurate determination of the gel point as the crossing point, and accordingly of n and t_c at all concentrations. Values of n and t_c thus determined are given in Table I.

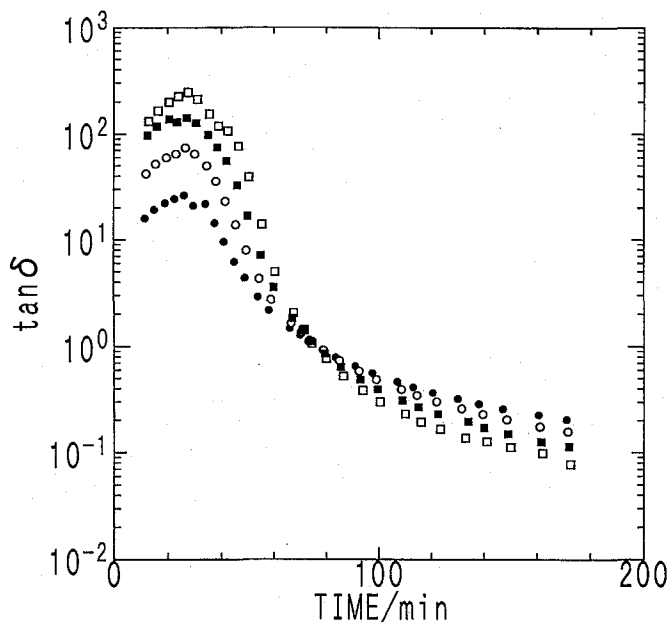


Fig. 3. Time evolution of $\tan \delta$ of the 80 wt% HTPB solution at four angular frequencies of $\omega=2.08$ (\square), 7.56 (\blacksquare), 27.5 (\circ), and 99.9 (\bullet). Four curves meet at the critical time t_c .

Table I. Experimental results at the gel point.

wt%	Sample code	t_c (min)	$\tan \delta$	n
30	DESOH301	430	1.80	0.68
40	DESOH403	240	1.65	0.65
50	DESOH501	160	1.50	0.63
60	DESOH601	110	1.30	0.58
80	DESOH801	76	1.05	0.52

The time dependence of $\tan \delta$ in Figures 2 and 3 suggests that viscoelastic properties of the system through the gelation process can be separately discussed by dividing the curves into three regions; the region 1 where $\tan \delta$ increases with the reaction time and reaches to a maximum; the region 2 where $\tan \delta$ after the maximum decreases with t , rapidly at high ω to the gel point; the region 3 beyond the gel point. In the region 1, all the solutions are essentially viscous liquids at room temperature so that the behavior of $G' \sim \omega^2$ and $G'' \sim \omega^1$ is clearly observed, and the steady viscosity gradually increases with t . It is inferred that higher molecular weight polymer chains with small number of branches are produced by end-linking in this region. In the region 2, the solutions are not viscous fluids any longer due to formation of large clusters and the steady viscosity increases very rapidly compared to the region 1. Enhancement in elasticity of the solution is much faster than an increase in η so that $\tan \delta$ may decrease. The region includes the critical region before the gel point. At the gel point, at least the largest cluster must be fully developed from one side to the other side of the sample volume. In the region 3 beyond the gel point, therefore, all samples behave elastically. The G_{eq} becomes larger and larger with t , and

may be used as a quantity which characterizes further development of a three-dimensional structure.

In comparing t dependence of $\tan \delta$ of the two samples in the region 2, we notice that the decrease in $\tan \delta$ is sharper for the 30 wt% solution. The distance from the gel point is usually measured by $\epsilon = |t - t_c|/t_c$. The t_c of the 30 wt% HTPB solution is larger than that of the 80 wt% solution by about a factor of five. Therefore the critical region scaled by ϵ surely becomes narrower with dilution.

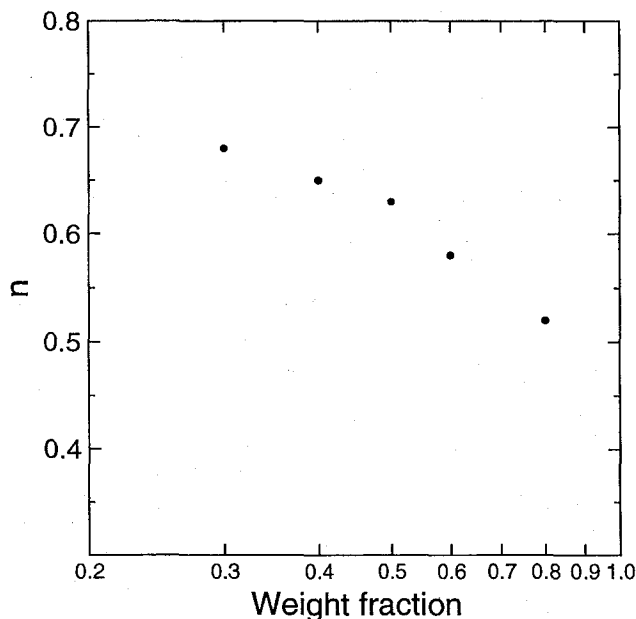


Fig. 4. A plot of the exponent n against polymer weight fraction w_f of the prepolymer solutions.

Figure 4 gives a plot of the exponent n against polymer weight fraction. The n increases with dilution from 0.52 at $w_f=0.80$ to 0.68 at $w_f=0.30$. In a previous study¹⁸⁾ on gelation of end-linking poly (propylene oxide) solutions, we found that n took a constant value of 0.66 ± 0.02 irrespective of molecular weight and concentration of prepolymer solutions whenever they are unentangled, and n decreased down to 0.51 ± 0.02 with increasing entanglement density. Since molecular weight between entanglements is about 2,000 for polybutadiene, the 80 wt% solution is slightly entangled. Thus the small n value of 0.52 may be due to the entanglement effect. The increase in n with dilution is possibly attributed to the side reaction of the isocyanate group with a water molecule in the atmosphere, which finally leads to formation of the urea group between two isocyanate groups. Inactivation of the isocyanate groups during the gelation process, becoming more effective with dilution, results in imbalanced chemical reaction of $r = [\text{NCO}]/[\text{OH}]$ less than unity. The fractal dimension d_f for less branched structures at the gel point is smaller than 2.5, and accordingly n becomes larger than that for $r=1$.¹⁹⁻²⁸⁾ The experiment under argon atmosphere is under progress to examine the universality of the n value.

The gelation time t_c is logarithmically plotted against polymer weight fraction w_f in Figure 5.

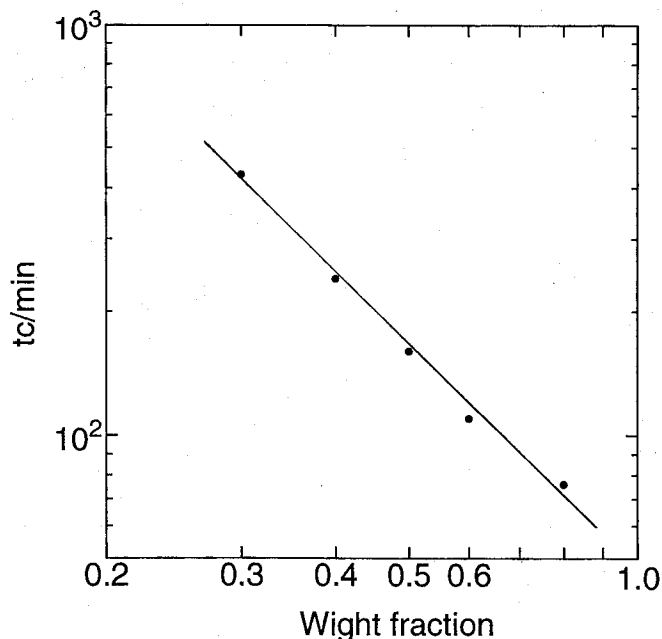


Fig. 5. A plot of the critical gelation time t_c against w_f . The solid line with a slope of -1.9 is empirically drawn.

The w_f dependence of t_c can be approximately represented by a straight line of the slope of -1.9 ± 0.1 . Recently Hakiki et al.²⁹⁾ measured the extent of chemical reaction, p , of OH-terminated polystyrene with DREF using the FT-IR technique, and showed that the chemical reaction proceeded by the second-order scheme up to $p=0.75$ which was close to the critical value at the gel point. If the second-order scheme is also applicable for the system of HTPB and DRFE, simple calculation predicts that t_c should be proportional to w_f^{-1} . The disagreement suggests that the chemical reaction in our system is not a reaction-limited one but may be a diffusion-controlled one, i.e., the reaction rate constant decreases with an increase in viscosity with p .

3.2 Viscoelastic behavior in the critical region

As was stated in Introduction, the critical gel can be discussed in terms of the two exponents k and z appearing in eqs. (1) and (2). We could measure the steady viscosity deeply in the critical region for only one solution with $w_f=0.40$, to which k was estimated as 1.25. On the other hand, growth of G_{eq} in the critical region could be observed for four solutions with w_f from 0.3 to 0.6 as is shown in Figure 6. The ϵ dependence of G_{eq} for $\epsilon < 0.6$ can be represented by the power law of eq. (2) and the exponent z seems to increase gradually with dilution from 1.8 ± 0.1 to 1.95 ± 0.1 . Universal values of k and z obtained for end-linking poly (propylene oxide) system were 1.0 ± 0.1 and 1.9 ± 0.1 . The k values are different between these two systems, whereas the z values are likely to be in agreement. Since the side reaction occurred in gelation of end-linking polybutadiene, it might be too early to conclude that values of n , k , and z may be different for different species of polymers, i.e., the universality does not hold.

The scaling theory^{11,13)} interrelates the three exponents by eq. (4)

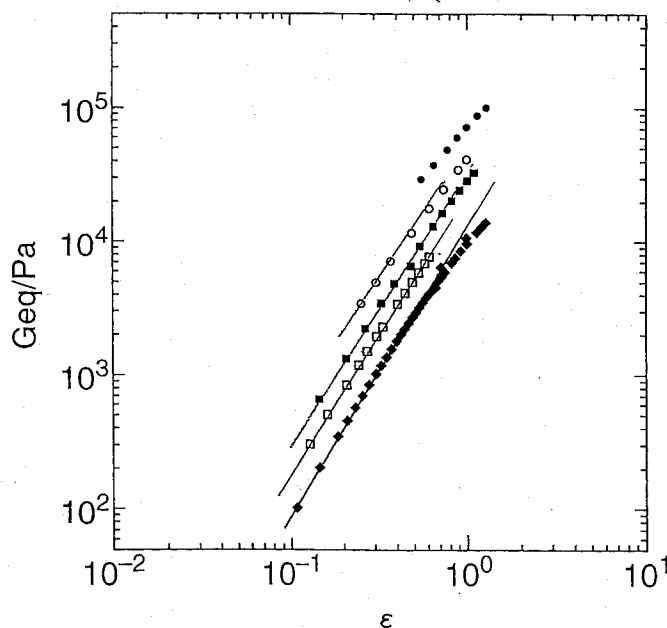


Fig. 6. The equilibrium shear modulus G_{eq} is plotted against ϵ . Symbols for w_f are: (◆) 0.3, (□) 0.4, (■) 0.5, (○) 0.6, and (●) 0.8.

$$n = z/(k+z) \quad (4)$$

From $k=1.25$ and $z=1.85$ for the 40 wt% solution, we calculate $n=0.60$ by eq. (4), which is different from the corresponding value of $n=0.65$ given in Table I.

4. ACKNOWLEDGEMENT

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